PROJECT TITLE : ANALYTICAL INVESTIGATIONS

PERIOD COVERED : JUNE 18 - JULY 23, 1981

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TRIACETIN (FMO)

The two triacetin samples, one from Bergen op Zoom and the other from FTR submitted by QC (1) and extensively investigated last month (2) were fingerprinted by headspace analysis on CW 400 (column : 50 m x 0.42 mm, i.d., glass) at 50 to 110°. The peak patterns of the readily volatile fraction (bath temp. 80°) of both the Bergen op Zoom and the FTR samples were identical. However, the concentration of an unknown compound (RT 8.31 min) present in both samples was found to be higher in the sample from Bergen op Zoom than in the FTR triacetin sample (3).

A more detailed study of the particularly volatile substances in various triacetins by headspace analysis has been started.

REACTION FLAVOUR (FMO/JJP)

Work has been initiated to fingerprint the chemical composition of volatile flavour components in reaction flavour mixtures by static headspace analysis in order to assign chemical composition to subjective screening data and to check the reproducibility of the reaction flavour preparation. Five flavour samples coded P-13/1, P-15, P-16/1, P-17/1, C-38/2 and one flavour treated cigarette sample plus control were fingerprinted. Chromatograms of samples P-13/1 and P-16/1 are given in Figures 1 and 2. The initial results seem encouraging.

LC profiling of non-volatiles (sugars, Amadori compounds, etc.) in various reaction flavour samples was initiated.

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CONDENSATE QUALITY CONTROL (FMO)

A simple and rapid analytical procedure for monitoring the reproducibility of the quality of dry condensate prepared for biological tests is currently being evaluated (4). Fifteen condensate samples were subjected to headspace analysis. Ten of them were prepared from the same cigarettes and were therefore identical. Based on fingerprint chromatograms all identical condensate samples were assigned correctly. A typical fingerprint chromatogram of a condensate sample is given in Fig. 3.

SUGAR ANALYSIS (JJP)

Sets of experimental cigarettes were analysed for glucose, fructose and saccharose by HPLC (5). No other sugars were detected in significant quantities.

An alternative method for glucose, fructose, saccharose, lactose, maltose and arabinose was set up to perform the same analysis by double derivatization and quantitation by gas chromatography (6) (Fig. 4). The results were found to concur well with the HPLC determinations for glucose, fructose and saccharose.

WS-14 (JJP)

GC equipment and an analytical procedure for analysing WS-14 was set up (7).

MH-30 (ETL)

The reaction products obtained by the derivatization of maleic hydrazide with dimethyl sulfate (8) were screened for possible isomers of 1-methyl-3-methoxy-pyridazone-(6). The crude reaction mixture was investigated by GC^2 (fused silica, 50 m x 0.3 mm, SP 2100, 150°) and GC^2/MS.

The main reaction product is 1-methyl-3-methoxy-pyridazone-(6) of mp. 49-51° (yield 78-85%) (9). The isometric 1.2-dimethyl-pyridaz-dione-(3.6) of mp. 128° (Lit. 135° (10)) is formed in ~10% yield. The compound was identified by GC^2/MS (140 (M^+, 73), 112 (15), 82 (82), 54 (37) and 43 (100) m/e) and compared with

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an authentic sample prepared from sym. dimethylhydrazine dihydrochloride and maleic anhydride (10). The 3.6 dimethoxy-pydidazine isomer (mp. 108°) could not be detected and is obviously not formed under the reaction conditions used for derivatisation of maleic hydrazide.

N-NITROSAMINES (FMO/ETL)

N-Nitrosoanabasine (NAB) has definitely been detected in cigarette mainstream and sidestream smoke by GC/TEA (11) and positively identified by GC/MS by comparison with an authentic sample. NAB is separated from other tobacco specific nitrosamines on 10% SP 2100 Supelcoport 100-120 mesh (column : 2.6 m x 2 mm, i.d. glass) at 205° and 40 ml He/min (Fig. 5). Under HPLC/TEA (12) as well as GC/TEA conditions, used so far for quantitation of NNN, NAtB and NNK, N-nitrosoanabasine (NAB) were eluted together with either NAtB (12) or NNN. This means that values reported in the literature for NNN and NAtB are probably falsified by the presence of NAB.

A sample of unknown composition submitted by the University of Neuchatel was analysed for nitrosamine content by GC/TEA and GC^2/MS.

Ten tobacco extract samples from the Pilot Plant (Project LEAR) were analysed for NNN, NAtB, NNK and DMN/NPY.

Serious problems with the GC/TEA have delayed investigations of various samples submitted by Biotechnology, Product Development and Product Research. The GC/TEA equipment is now functional.

ETNA / ONNENS (FMO)

CO, CO_2, NO, NO_2, nicotine, ammonia, humidity, temperature and particles (number and size) in exhaust gases of ETNA production were monitored during the period of July 7 to 15, 1981 (13).

NITRITE REMOVAL (MUM)

A model system was used to investigate the removal of nitrite by urea under various pH and temperature conditions (14). The results indicate a rapid and complete nitrite decomposition in the presence of urea under acidic conditions according to :

$$2HNO_2 + H_2NCONH_2 \longrightarrow 3\ H_2O + CO_2 + 2\ N_2$$

Decomposition is less rapid in citric acid than in phosphoric acid solutions. Nitrite decomposition is slightly faster at 30° than at 22°C.

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Experiments with Burley strip extracts and with Burley stems confirmed the results of the model system.

Nitrite and nitrate were monitored simultaneously by HPLC on an anion exchange column with UV detection at 210 nm. Nitrate alone was measured by a specific ion electrode.

OTHERS

- Routine analyses were performed on potassium, calcium, magnesium (24 samples), phosphate, sulfate (70 samples), and alcohols (10 samples).
- CF was analysed in 20 German brands for Product Development.
- Periodic checks of the recovery of DMN in nitrosamine determinations after the clean-up procedure using ^{14}C DMN were performed.

REPORT WRITTEN

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Fink-W.

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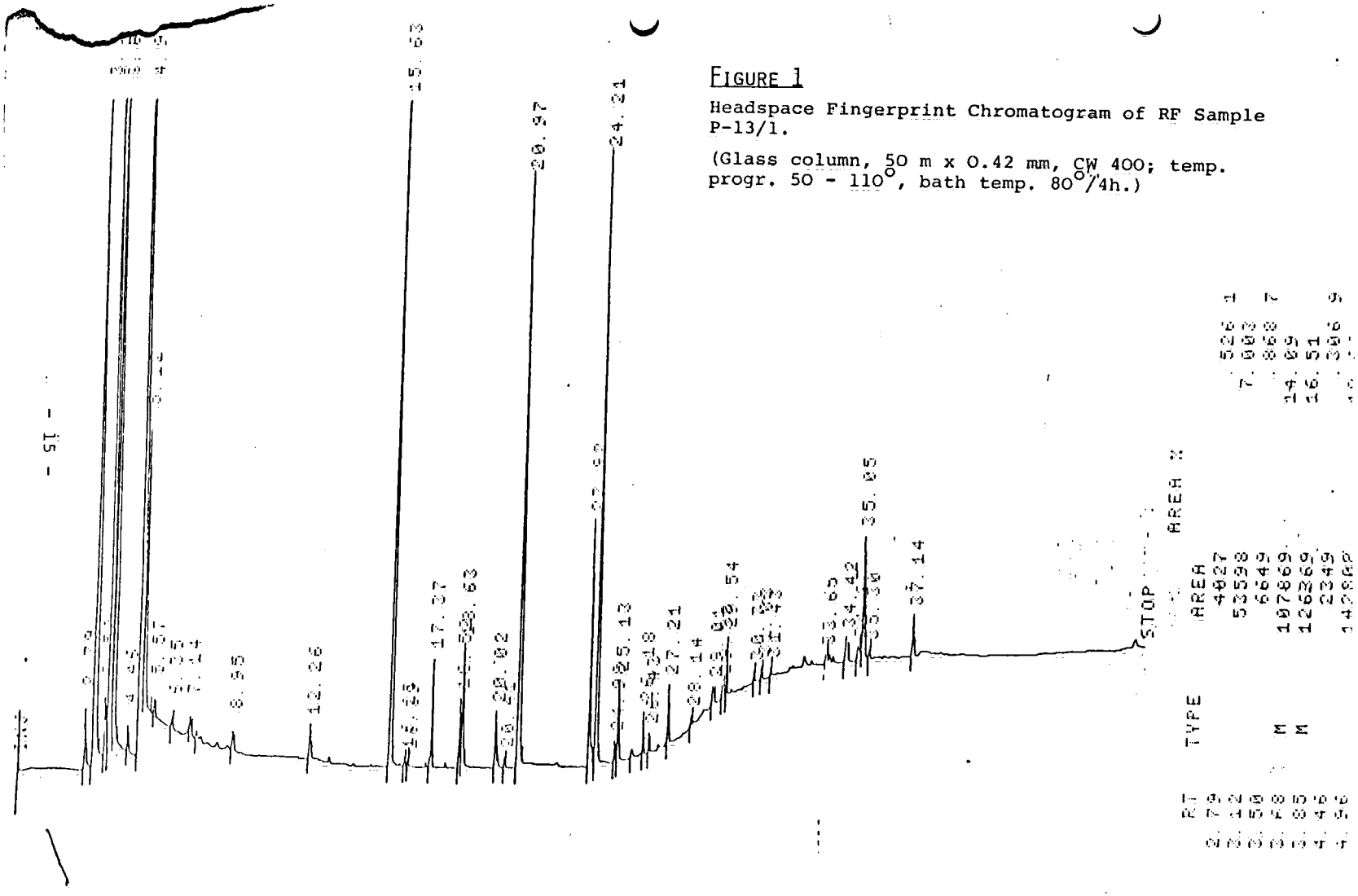

FIGURE 1

Headspace Fingerprint Chromatogram of RF Sample P-13/1.

(Glass column, 50 m x 0.42 mm, CW 400; temp. progr. 50 - 110°, bath temp. 80°/4h.)

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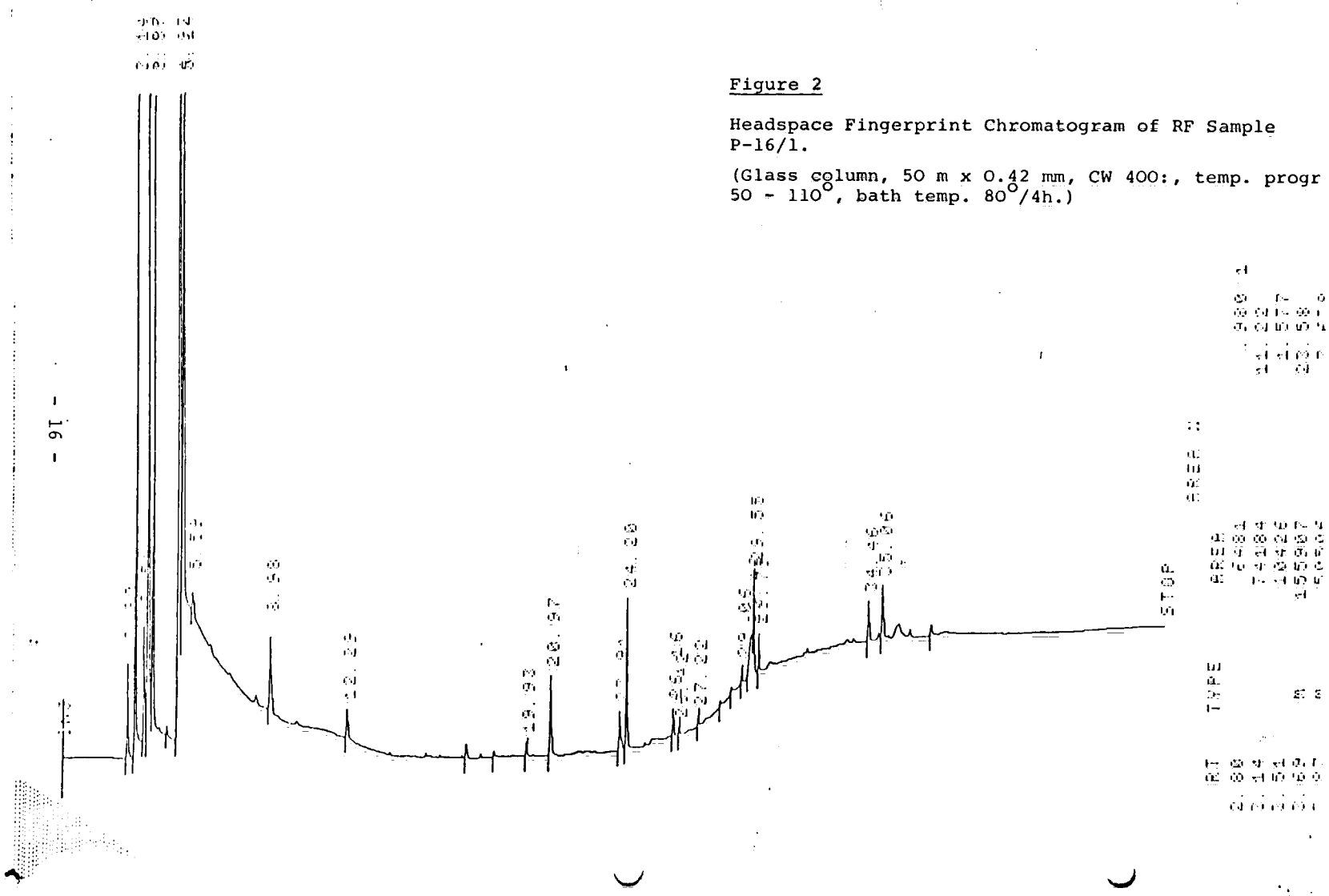

Figure 2

Headspace Fingerprint Chromatogram of RF Sample P-16/1.

(Glass column, 50 m x 0.42 mm, CW 400:, temp. progr 50 - 110°, bath temp. 80°/4h.)

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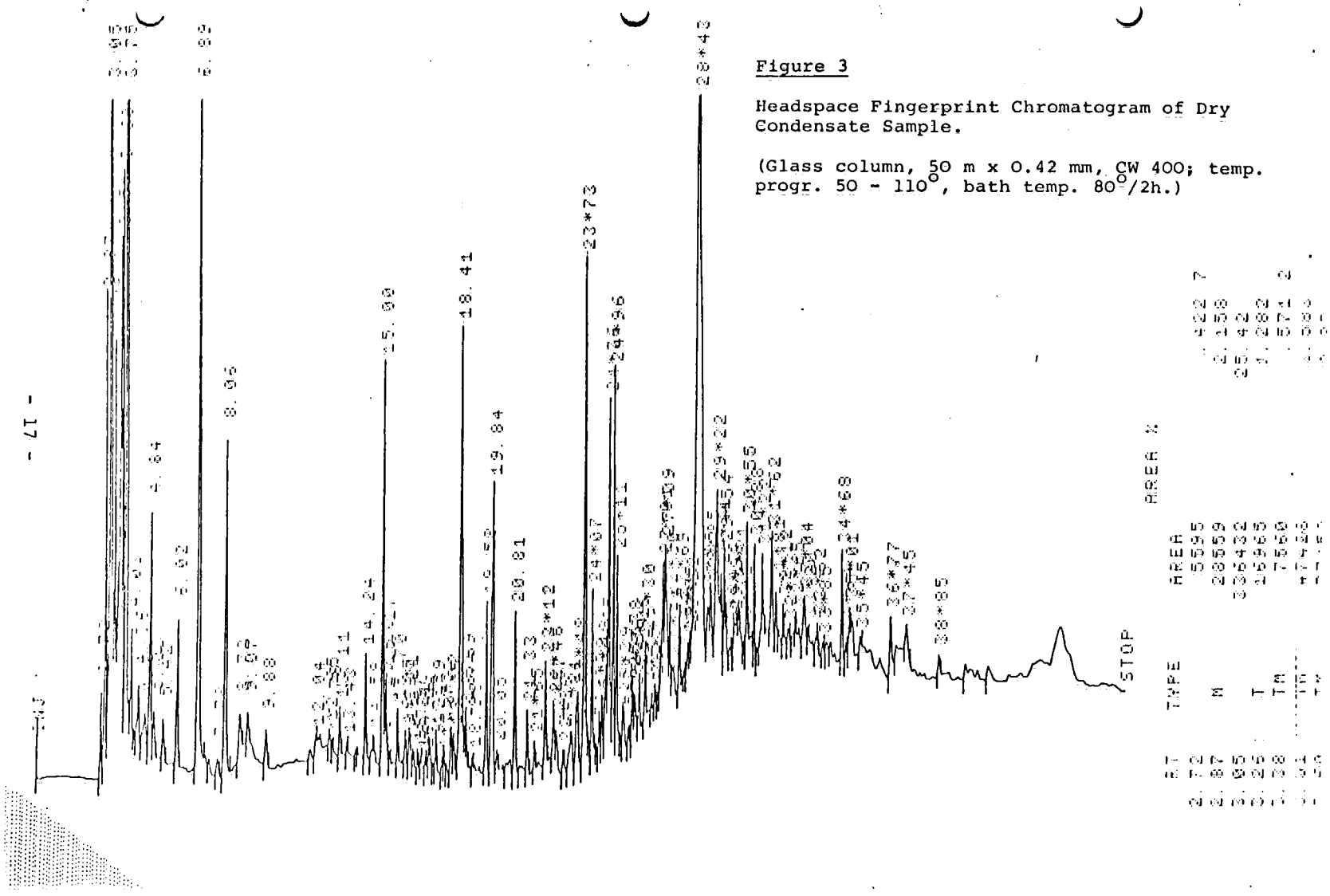

Figure 3

Headspace Fingerprint Chromatogram of Dry Condensate Sample.

(Glass column, 50 m x 0.42 mm, CW 400; temp. progr. 50 - 110°, bath temp. 80°/2h.)

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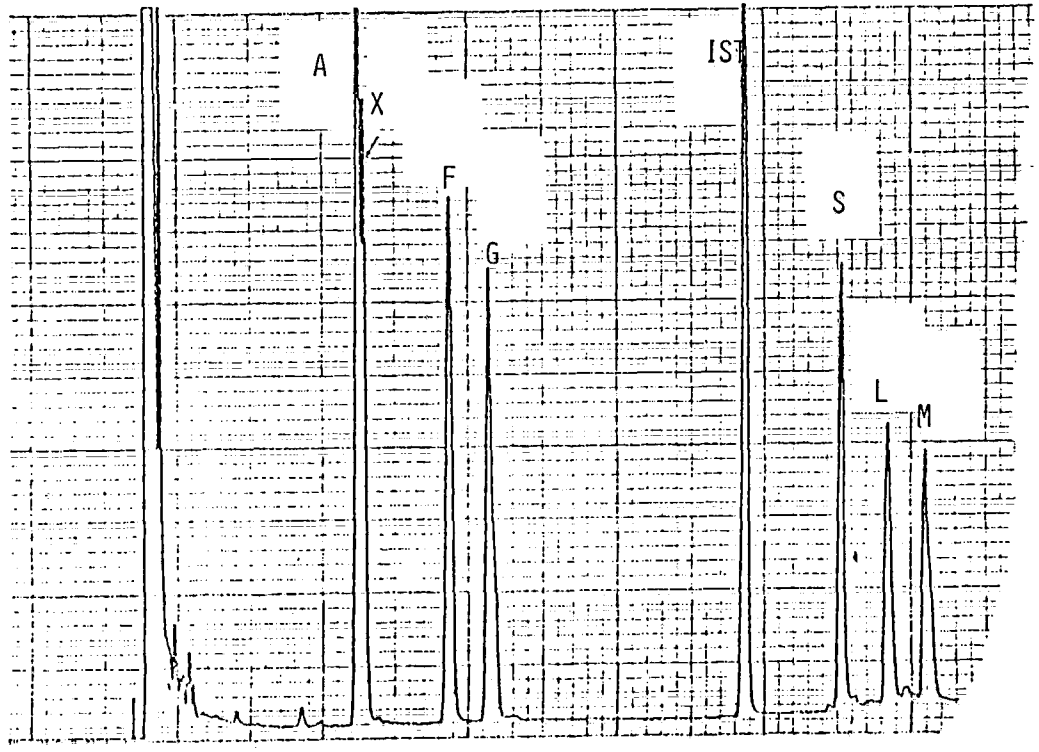
Figure 4

Gas Chromatographic Separation of a Synthetic Mixture of Arabinose (A), Xylose (X), Fructose (F), Glucose (G), Saccharose (S), Lactose (L) and Maltose (M).

(3% SP 2250 on Supelcoport 100 - 120; Temp. Progr. 150 - 290, 6°/min.)



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